

NBSIR 76-1002

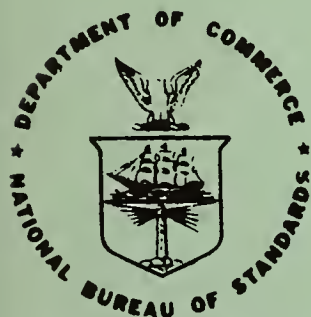
Industrial Process Data for Fluids: A Survey of Current Research at the National Bureau of Standards

Howard J. White, Jr., Editor

Office of Standard Reference Data
National Bureau of Standards
Washington, D. C. 20234

April 1976

Summary Report



**U S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS**

NBSIR 76-1002

**INDUSTRIAL PROCESS DATA FOR
FLUIDS: A SURVEY OF CURRENT
RESEARCH AT THE NATIONAL
BUREAU OF STANDARDS**

Howard J. White, Jr., Editor

Office of Standard Reference Data
National Bureau of Standards
Washington, D. C. 20234

April 1976

Summary Report

U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, *Secretary*
James A. Baker, III, *Under Secretary*
Dr. Betsy Ancker-Johnson, *Assistant Secretary for Science and Technology*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Acting Director*

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT, KEY WORDS	1
INTRODUCTION	2, 3
RESEARCH PROJECTS	
1. Properties of Cryogenic Fluids	4, 5, 6
2. Hydrogen/Oxygen Properties	7
3. Fluid Transport Properties	8, 9
4. Properties of Cryogenic Fluid Mixtures	10, 11
5. Development of Cryogenic PVT Algorithms for Space Applications	12, 13
6. Thermophysical Properties Data for Pure Components of LNG Mixtures	14, 15, 16, 17
7. Densities of Liquefied Natural Gas Mixtures	18, 19
8. LNG Density References System	20, 21
9. Heating Value of Flowing LNG	22
10. LNG Fuels Safety	23, 24
11. Energy Conservation Potential in the LNG Industry	25, 26
12. Survey of Current Literature on LNG and Methane	27, 28
13. Cryogenic Data Center Information Services	29, 30
14. Analysis, Evaluation, and Compilation of Chemical Thermodynamic Data	31, 32
15. Thermodynamic Data on Organic Compounds	33, 34
16. Joint Industry-Government Project on the Thermophysical Properties of Ethylene	35, 36
17. Excess Property Data for Binary Liquids	37, 38
18. Thermal Conductivity of Selected Substances	39, 40, 41

TABLE OF CONTENTS

	<u>Page</u>
RESEARCH PROJECTS (continued)	
19. Transport Properties of Fluids in the Critical Region	42, 43
20. Thermodynamic Properties of Fluids	44, 45
21. Thermodynamic Properties of Fluids in the Critical Region	46, 47, 48
22. PVT Relations in Gases	49

Industrial Process Data for Fluids: A Survey
of Current Research at the National Bureau of Standards

Howard J. White, Jr., Editor

ABSTRACT

This report summarizes current activities sponsored by three groups within the National Bureau of Standards that are involved with the production of industrial process data for fluids. The three groups involved are the Cryogenics Division, the Equation of State Section of the Heat Division, and the Office of Standard Reference Data; other organizations in NBS and outside are also involved in various ways.

The report takes the form of a listing of projects with some detailed information about each. Some of the projects are designed to provide industrial process data directly. Others systematically cover types of data that are of continual utility in industrial process calculations with the result that the data produced will be used for industrial purposes as well as for other purposes. A few of the projects attack problem areas that must be resolved before proper industrial process data in the area can be obtained. All of the projects focus on quantitative numerical data obtained for direct measurement, critical evaluation of data from the literature or theoretical estimation or calculation.

This report has been prepared to show interested readers the interrelationships within a set of projects that might otherwise pass unnoticed because different organizational units within NBS are involved. Continued interaction between the program managers involved leads to interactions between the projects so that the listing is not a listing of independent unreacting projects but rather a listing of interacting projects following broad programmatic lines.

KEY WORDS

Industrial process data; project summaries;
quantitative numerical data.

INTRODUCTION

This report summarizes the current status of a set of projects being carried out under the program management of the National Bureau of Standards. Each of the projects included in the set is concerned with the generation of data of a type widely used in industry.

Taken collectively, the projects involve data compilation and evaluation, experimental measurements and theoretical developments; they reach across organizational bounds within NBS and include activities being carried on outside of NBS. They have been collected here because together they indicate a programmatic thrust which might not be evident from a consideration of the NBS program as a whole or as listed along organizational lines. A further justification for collecting them lies in the fact that the programs of which these projects are parts are sufficiently coordinated that there is substantial interaction between projects and the collection is not simply a listing of independent entities.

The projects included are concerned with the thermodynamic and thermophysical properties of fluids. The fluids under consideration are single substances that are gases or relatively volatile liquids in the vicinity of room temperature or are mixtures of these. The properties under consideration fall into three broad types: the chemical thermodynamic properties, those properties needed to characterize chemical equilibria; the PVT and related physical thermodynamic properties, those properties needed to characterize the equilibrium behavior of chemically stable systems as a function of temperature, pressure, and composition; and the transport properties, those properties needed to characterize the flow of matter and energy in systems not in physical equilibrium. Data of these types are used in industrial calculations such as are involved in process and equipment design, optimization of reactor conditions, product purification, process control, pollution and hazard control, intermediate and product analysis and custody transfer. The industries to which the data involved can be expected to be of most interest are the chemical, petrochemical, petroleum, gas and gas transmission industries.

It should be stressed that the projects selected do not include all NBS projects on fluids as defined above, all projects involving thermodynamic or thermophysical properties, nor all projects that will produce data of interest to industry. They do represent a substantial effort with a common technical base and a certain commonality of purpose.

The relevance of the types of data concerned to industrial needs has been stated. However, something more might be said about the

relevance of the individual projects. The application of some projects is evident from inspection of their descriptions. The direct importance of others is obvious from their industrial sponsorship. But, there is a third group of projects whose relevance is only revealed by broader considerations. The numbers of substances, the ranges of concentrations, temperatures and pressures for which data are now, or will soon be needed, are innumerable. There is no possibility for a program of direct measurement to fill all such needs. Methods are needed to interpolate and extrapolate over ranges of temperature and pressure, to relate the properties of mixtures to those of their components, to use one set of properties of a substance to estimate others and, ultimately, to estimate the properties of a substance from those of chemically related substances. Accompanying this need for such methods is a need for selected data of high quality for use in verifying the methods developed and to provide the framework on which the network of estimating techniques must be based. It is to the building of this network of techniques and reference data that the third group of projects is directed.

Industrial time pressures are such that, if data are not available, they are estimated; if an accurate estimation technique is not available, a crude one is used. The price for the gaps and crudities in our current network of reference data and estimation techniques is paid in occasional spectacular failures and in thousands of inefficiencies, some obvious in retrospect, some still hidden. The relationships between cause and effect are usually subtle. Industrial organizations support projects in those areas where lack of a particular type of data can be seen to be handicapping their efforts. Some of these projects are proprietary; others are supported on a joint or industry-wide basis. Examples of the latter type exist in this report. However, the development of a satisfactory network of estimation techniques and reference data is a task too large in size and too pervasive in effect to be supported industrially on a specific project basis. Recognition of the importance of this task and the need for government leadership is one of the reasons for the preparation of this report.

Responsibility for the preparation of this report and for a number of the projects reported herein lies with four groups in NBS--the Cryogenic Data Center of the Cryogenics Division, the Properties of Cryogenic Fluids Section of the Cryogenics Division, the Equation of State Section of the Heat Division, and the Office of Standard Reference Data. Inquiries on material included in this report may be directed to Mr. Neil Olien, Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado 80302 (Telephone 303 499-1000, Ext. 3257); or to Dr. Howard J. White, Jr., Office of Standard Reference Data, National Bureau of Standards, Washington, D. C. 20234 (Telephone 301 921-2581).

1. Title. PROPERTIES OF CRYOGENIC FLUIDS

Principal Investigators. G. C. Straty and D. E. Diller
NBS, Boulder, Colorado 80302

2. Cost Center Number. 2750141

3. Sponsor. NBS

4. Introduction. Accurate thermophysical properties data and predictive calculation methods for cryogenic fluids are needed to support advanced cryogenic technology projects. For example, liquefied natural gas is expected to supply an increasing percentage of the United States' energy requirements through 1990. Liquefaction plants, ships and receiving terminals are being constructed to transport and store natural gas in the liquid state (LNG). Accurate thermophysical properties data for LNG are needed to design low temperature processes and equipment. Accurate data will benefit the energy industries and the consumer by providing for safe and efficient operations and reduced costs.

5. Objectives or Goals. The objectives of this project are to provide comprehensive accurate thermodynamic, electromagnetic and transport properties data and calculation methods for technically important compressed and liquefied gases (helium, hydrogen, oxygen, nitrogen, methane, ethane, etc.) at low temperatures. Precise compressibility, calorimetric and other physical property measurements will be performed to fill gaps and reconcile inconsistencies. Definitive interpolation functions, computer programs and tables will be prepared for engineering calculations. The immediate goals of this work are to obtain accurate sound velocity and thermal diffusivity data for compressed and liquefied gases by using laser light scattering spectroscopy techniques. Sound velocity data are useful for testing the consistency of volumetric, calorimetric and thermodynamic properties data, and are potentially useful for density gauging applications. Thermal diffusivity data are required for performing thermodynamic and heat transfer calculations.

6. Background. When light is incident on a perfectly homogeneous fluid, the reradiated (scattered) light field sums to zero in all but the exact forward direction. For a "real" fluid, however, fluctuations, arising through various mechanisms, destroy the perfect homogeneity and results in the scattering of light in other directions as well. For example, thermally activated density fluctuations (phonons), propagating with the characteristic velocity of sound, give rise to scattered light which is Doppler shifted in frequency from the incident light frequency and whose spectrum contains information on the sound velocity and attenuation. Local non-propagating temperature fluctuations, which decay diffusively, give rise to scattered light in a narrow frequency band about the incident light frequency and whose spectrum

contains information on the lifetime of the fluctuations (thermal diffusivity). Since the frequency shifts are generally very small, it was not until the advent of the lasers with their extremely well defined frequency, that practical experiments using these phenomena were possible.

The application of laser light scattering techniques to obtaining thermophysical properties data was initiated to complement and check other measurement methods and to solve measurement problems inherent in more conventional methods. For example, laser light scattering techniques permit measurements of sound velocities for fluids and under conditions for which sound absorption is too large to perform ultrasonic measurements; laser light scattering techniques permit measurements of thermal diffusivities under conditions for which convection interferes with measurements of thermal conduction. The feasibility of light scattering experiments to obtain data on binary diffusion coefficients has also recently been demonstrated.

7. Program and Results. An apparatus has been assembled for laser light scattering spectroscopy on compressed and liquefied gases (76 - 300 K, 350 bars). The apparatus consists of a high pressure optical cell, a cryostat for refrigeration with liquid nitrogen, an argon ion laser, low-level light detection equipment, a pressure scanned Fabry-Perot interferometer, and a commercial digital correlation function computer.

The light scattered from fluctuations in the fluid can be analyzed with either digital autocorrelation techniques for the examination of the very narrow lines associated with scattering from temperature fluctuations (Rayleigh scattering) or with a pressure scanned Fabry Perot interferometer for the measurement of the Doppler frequency shifts associated with the scattering from propagating density (pressure) fluctuations (Brillouin scattering).

Data on the hypersound velocities in pure methane have been obtained by Brillouin scattering techniques at low densities ($< 14 \text{ mol/l}$) where the large sound absorption in methane prohibits more conventional ultrasonic measurements. Data have been obtained along several isotherms from 210 K to 300 K at densities down to 1 mol/l . Agreement with previously measured ultrasonic velocities in the regions of overlapping data is good. The data have been combined with previously measured PVT data to obtain the isentropic compressibility and ratio of the specific heats. A manuscript reporting the results of these measurements has been prepared and submitted to Cryogenics for publication.

We have completed equipment modifications to permit the determination of the thermal diffusivity, $\lambda/\rho C_p$, of compressed and liquefied gases, including the critical region. The most accurate method for doing this is to use photon-counting and digital autocorrelation techniques to measure the temporal behavior of the spontaneous temperature fluctuations occurring in the fluid which is governed by the bulk fluid thermal diffusivity. This is equivalent to measuring the very narrow Rayleigh line width and requires a resolution of about one part in 10^{12} .

Preliminary checks of the modified apparatus on a well-characterized test fluid appear to have been satisfactory. Preparations for thermal diffusivity measurements on liquefied methane are in progress.

1. Title. HYDROGEN/OXYGEN PROPERTIES
Principal Investigator. L. A. Weber,
NBS, Boulder, Colorado 80302
2. Cost Center Number. 2750547
3. Sponsor. NASA (Lewis Research Center)
4. Introduction. Comprehensive accurate thermophysical properties data for compressed and liquefied hydrogen and oxygen at high pressures (up to 100 MPa (15,000 psi)) are needed to support NASA's advanced chemical propulsion system development program.
5. Objectives. The purpose of this project is to provide NASA with accurate thermodynamic properties data for hydrogen and oxygen at high pressures (5000-15,000 psi) and at temperatures encountered in developing and testing space shuttle propulsion systems. The goal for our immediate work is to perform high precision PVT measurements on gaseous and liquid oxygen (55-300 K) at pressures up to 12,000 psi (827 bar) and calculate accurate thermodynamic properties data (entropy, internal energy, enthalpy).
6. Background. During the period 1958-1970 the NBS Cryogenics Division provided comprehensive accurate thermophysical properties data for compressed and liquefied hydrogen and oxygen at pressures to 35 MPa (5000 psi) in support of NASA's propulsion system development program. Advanced propulsion systems now being developed will use these fluids at higher pressures. The thermophysical properties data base is now being extended from 5000 psi to 15,000 psi to provide measurements and calculation methods sufficient for all foreseeable engineering calculations.
7. Program and Results. Preparations for new equation of state (PVT) measurements on compressed and liquefied oxygen at pressures to 82.7 MPa (12,000 psi) are in progress.

1. Title. FLUID TRANSPORT PROPERTIES
Principal Investigator. Howard J. M. Hanley
NBS, Boulder, Colorado 80302
2. Cost Center Number. 2750124
3. Sponsor. NBS-Office of Standard Reference Data
4. Introduction. Methods for predicting the transport properties of fluid mixtures are unreliable and data are scarce. Prediction methods are needed, however, to supply the necessary design data needed to increase efficiency and reduce costs.
5. Objectives or Goals. The long range or continuing goal of the program is to perform a systematic study of the theories and experimental measurements relating to transport properties, specifically the viscosity and thermal conductivity coefficients, of simple mixtures over a wide range of experimental conditions. The specific objectives of the program include: 1) the systematic correlation of the transport properties of simple binary mixtures and the development of prediction techniques, 2) development of a mixture theory for the dilute gas region and the dense gas and liquid regions, 3) extension of the theory and prediction techniques to multicomponent systems, and 4) suggested guidelines for future areas of experimental work.
6. Background. A continuing program has successfully expanded the state-of-the-art of transport phenomena for pure fluids. Information for pure fluids is required as a prerequisite for mixture studies. The theory of transport phenomena has been developed and applied to produce practical numerical tables of the viscosity, thermal conductivity and diffusion coefficients of simple fluids: Ar, Kr, Xe, N₂, O₂, F₂, He, H₂, CH₄. Recent work has extended this approach to ethane. It is felt that a successful mixture program will emerge from combining the results for pure fluids with equation of state studies. The equation of state work is being carried out by other investigators in this laboratory.
7. Program and Results. Statistical mechanics has been applied to predict and correlate the dilute and moderately dense thermophysical properties of carbon dioxide¹. Carbon dioxide was selected as a typical polyatomic molecule. The self-diffusion coefficients of methane have been correlated and tabulated². Results for the dilute gas transport properties of oxygen and nitrogen have been published³. The well-known critical point anomaly in the thermal conductivity can now be predicted to within experimental error⁴. An equation to calculate the dense gas and liquid transport properties of several simple fluids has been reported⁵. Preliminary work on the transport properties of mixtures has been very promising. Theoretical studies on transport theory have been reported⁶.

References

1. J.F. Ely and H.J.M. Hanley, Mol. Phys. 30, 565 (1975).
2. K.R. Harris, H.J.M. Hanley, et al., "The Self-Diffusion of Simple Fluids," Australian National Univ. Press., DRU-RR 2 (1974).
3. H.J.M. Hanley and J.F. Ely, J. Chem. Phys. Ref. Data 2, 735 (1973).
4. H.J.M. Hanley, J.V. Sengers and J.F. Ely, Proc. 14th Int. Conf. Thermal Conductivity (Pergamon Press, 1975).
5. H.J.M. Hanley, W.M. Haynes and R.D. McCarty, Cryogenics 15, 413 (1975); J. Chem. Phys. Ref. Data 3, 979 (1974).
6. For example, H.J.M. Hanley and W.M. Haynes, J. Chem. Phys. 63, 358 (1975); H.J.M. Hanley and R.O. Watts, Physica 79A, 351 (1975).

1. Title. PROPERTIES OF CRYOGENIC FLUID MIXTURES
Principal Investigators. M. J. Hiza, A. J. Kidnay (part-time)
R. C. Miller (part-time), and W. R. Parrish (part-time)
NBS, Boulder, Colorado 80302
2. Cost Center Numbers. 2750142; 2750145
3. Sponsor. NBS; NBS (OSRD)
4. Introduction. Accurate thermodynamic properties data and predictive calculation methods for mixtures of cryogenic fluids are needed to design and optimize low temperature processes and equipment. This project provides new experimental measurements on equilibrium properties and compilations of evaluated equilibrium properties data which are suitable for direct technological use or for the evaluation of predictive calculation methods.
5. Objectives or Goals. The overall objectives of this project are to provide critically evaluated data, original and from other sources, on the phase equilibria and thermodynamic properties of cryogenic fluid mixtures. The program has been divided into the following elements:
 - a) Preparation of a comprehensive bibliography on experimental measurements of equilibrium properties for mixtures of selected molecular species of principal interest in cryogenic technology.
 - b) Selection and/or development of methods for correlation, evaluation and prediction of equilibrium properties data.
 - c) Retrieval and evaluation of experimental data for specific mixture systems selected on the basis of theoretical and/or technological importance.
 - d) Preparation of guidelines for future research based on the deficiencies noted in (a), (b), and (c).
 - e) Performing experimental research to alleviate deficiencies and provide a basis for improvement of prediction methods.
6. Background. A physical equilibria of mixtures research project was established in the Cryogenics Division in 1959. The initial effort, based on a bibliographic search and other considerations, was directed toward the acquisition of new experimental data on the solid-vapor and liquid-vapor equilibria and physical adsorption properties for a limited number of binary and ternary mixtures of components with widely separated critical temperatures. Most of the systems studied included one of the light hydrocarbon species--methane, ethane, or ethylene (ethene)-- with one of the quantum gases--helium, hydrogen, or neon. The data for these systems led to significant improvements

in the predictions of physical adsorption equilibrium and a correlation for the prediction of deviations from the geometric mean rule for combining characteristic energy parameters. In addition, significant new information was obtained for interaction third virial coefficients which was used in a correlation by one of our consultants, J.M. Prausnitz. The approach taken in this work has been as fundamental as possible with the intention of having an impact on a broad range of mixture problems.

Recent efforts have been directed toward problems associated with systems containing components with overlapping liquid temperature ranges, such as the nitrogen + methane system.

7. Program and Results. The recent progress of this program is summarized as follows:

- a) The comprehensive bibliography of fluid mixtures data entitled "Equilibrium Properties of Fluid Mixtures: A Bibliography of Cryogenic Data" has been published.
- b) Work is continuing on the compilation of liquid-vapor equilibrium data and derivation of the excess Gibbs functions and Henry's constants for binary systems containing methane with the light hydrocarbons, argon and nitrogen. A paper, "On the Consistency of Liquid-Vapor Equilibria Data for Binary Mixtures of Methane with the Light Paraffin Hydrocarbons," which covers a portion of this work, was presented at the 1975 Cryogenic Engineering Conference.
- c) A paper entitled "Liquid-Vapor Phase Equilibria in the System $N_2 + CH_4$ from 130.00 K to 180.00 K," has been published, Cryogenics 15, 531 (1975). This paper includes an evaluation of available data for this system, as discussed in (b), as well as the new measurements.
- d) New liquid-vapor equilibrium composition measurements at selected conditions for the methane + ethane system have been obtained and are being analyzed.

1. Title. DEVELOPMENT OF CRYOGENIC PVT ALGORITHMS FOR SPACE APPLICATIONS
Principal Investigators. R. D. McCarty and H. M. Roder
NBS, Boulder, Colorado 80302
2. Cost Center Number. 2750423
3. Sponsor. National Aeronautics and Space Administration, Johnson Space Center, Houston, Texas, Mission Planning and Analysis Division/FM-7.
4. Introduction. Cryogenic hydrogen and oxygen systems were used as the sources for the fuel cells during the Gemini, Apollo and Skylab programs. During these programs the stored cryogens became one of the main limiting consumables involving mission length. The critical nature of the cryogenic systems required very accurate premission analysis. Onboard monitoring of the cryogens was relatively inaccurate (5-10 percent) and required periodic updates from the ground. One of the major improvements in Space Shuttle operations will be the capability of monitoring consumables onboard accurately so as to reduce support requirements. Also, because of the expected frequency of flights a more efficient premission computational technique will be required.
5. Objectives or Goals. The objectives of this study are:
 - a. Develop a detailed equation of state for hydrogen based on the recently completed measurement program.
 - b. Develop density explicit equations over a limited pressure-temperature range for hydrogen, oxygen, nitrogen and ammonia. These equations will be used for both onboard computers (as a back-up quantity gaging system) and ground computer remote terminal operation.
 - c. Provide other thermodynamic and transport properties for ammonia in addition to the equation of state. The most important of these are the heat of vaporization and saturation temperature versus pressure.
 - d. Develop slush properties of oxygen and hydrogen. The area of work has application in space programs beyond Shuttle and in industry as well.

It should be pointed out that the culmination of these objectives will not only be in the analytical results, but also in the development of computer programs available for general use to NASA and industry. The basic intent of a study of this type is to provide data in such a form that they not only satisfy the NASA requirement, but will be adequate for a wide range of other users in government and industry.

6. Background. The Cryogenic Data Center provided the data and equations used for the cryogenic consumables during the Apollo and Skylab programs. The staff of the Center have developed an internationally recognized expertise in the statistical treatment of data and in the development and optimization of empirical equations of state for fluid properties. In addition the NBS-Cryogenics Division has produced the bulk of the available source data on the properties of hydrogen and oxygen by means of NASA-funded experimental programs. The most recent work involved measurement to extend the PVT properties of hydrogen from 35 to 100 MPa. The data are being used in the space shuttle main engine development. A corollary program was started to revise an existing equation of state for hydrogen to include these data. This effort was stopped short of the intended goal due to lack of funds. It is the intent of this project not only to complete that work, but to extend the techniques into an onboard computational capability.
7. Program and Results. An existing 32-term modified Benedict-Webb-Rubin (MBWR) equation of state for parahydrogen has been modified to fit the new, high pressure data to within the precision of the data. An equation of state has been provided as well as tables of properties for ammonia. The bulk of the effort has been expended on attempts to develop a functional form for an accurate, density explicit equation of state. Thus far, only one form has been found which even approaches the accuracy. This form, in essence, relates the actual density at a given pressure and temperature to a corresponding density on the saturated liquid and vapor lines. Final testing and optimization of the equation have not as yet been accomplished on parahydrogen.

1. Title. THERMOPHYSICAL PROPERTIES DATA FOR PURE COMPONENTS OF LNG MIXTURES

Principal Investigators. R. D. Goodwin, G. C. Straty, L. A. Weber, H. M. Roder, and R. Tsumura, NBS, Boulder, Colorado 80302.

2. Cost Center Numbers. 2750574 (2750364)

3. Sponsor. American Gas Association, Inc., Project BR50-10.

4. Introduction. Accurate phase equilibrium, equation of state (PVT), and thermodynamic properties data are needed to design and optimize gas separation and liquefaction processes and equipment. Accurate data for the pure components of LNG mixtures will permit developing comprehensive accurate predictive calculation methods which take into account the dependence of the thermophysical properties of mixtures on the composition, temperature, and density.

This project will provide comprehensive accurate thermophysical properties data and predictive calculation methods for compressed and liquefied hydrocarbon gases to support the development of LNG technology at NBS and throughout the fuel gas industry.

5. Objectives or Goals. The objectives of our work are the determination of comprehensive accurate thermophysical properties data and predictive calculation methods for the major pure components (methane, ethane, propane, butanes, and nitrogen) of liquefied natural gas mixtures at temperatures between 90 K and 300 K and at pressures up to 350 bar (5000 psi). Our goal is to provide a range and quality of data that will be recognized as definitive or standard for all foreseeable low temperature engineering calculations.

6. Background. Liquefied natural gas is expected to supply an increasing percentage of the United States' future energy requirements. It is likely that massive quantities of liquefied natural gas will be imported during the years 1976 - 1990. Ships and importation terminals are being built for transporting, storing, and vaporizing liquefied natural gas for distribution. Accurate physical and thermodynamic properties data for compressed and liquefied natural gas mixtures are needed to support these projects. For example, accurate compressibility and thermodynamic properties data are needed to design and optimize liquefaction and transport processes; accurate data for the heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition, are needed to provide a basis for equitable custody transfer.

Accurate thermodynamic properties data for liquefied gas mixtures must be based on precise compressibility and calorimetric measurements; compressibility data give the dependence of thermodynamic properties

on pressure and density (at fixed temperatures); calorimetric data give the dependence of thermodynamic properties on temperature (at fixed pressures and densities). It is impossible, however, to perform enough compressibility and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation of the data to arbitrary compositions, temperatures and pressures. Instead, thermodynamic properties data for multicomponent mixtures usually must be predicted (extrapolated) from a limited number of measurements on the pure components and their binary mixtures.

This project was initiated to provide the natural gas industry with comprehensive accurate data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. We have published National Bureau of Standards Technical Note 653, "Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar," by Robert D. Goodwin (April 1974). This report contains the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating thermophysical properties data for LNG mixtures.

7. Program and Results.

7.1 Melting Pressures, Vapor Pressures and Equation of State (PVT) Data--G. C. Straty and R. Tsumura.

Comprehensive accurate measurements of the melting pressures, vapor pressures and equation of state (PVT) for compressed and liquefied ethane, 90 - 320 K, 5000 psi, have been completed. Two reports have been submitted for publication:

- a) G. C. Straty and R. Tsumura, "Solid Ethane and the Melting Line," J. Chem. Phys. (in press, 1976).
- b) G. C. Straty and R. Tsumura, "PVT and Vapor Pressure Measurements on Ethane," J. Res. Nat. Bur. Stand. (in press, 1976).

7.2 Ethane, Dielectric Constant Data--L. A. Weber.

Previous dielectric constant data for ethane have been limited to the saturated liquid near the triple point and to the saturated liquid and vapor in the region of the critical point. New experimental work has been completed on the measurement of the dielectric constants of ethane as a function of temperature and density over a wide range of densities in the saturated and compressed fluid. The present data include the saturated liquid in the temperature range 95 - 300 K and seven isotherms at temperatures between 120 and 323 K and at pressures up to 390 bars. The capacitance measurements were made with a commercial three-terminal a-c bridge having a resolution of one part in 10^6 . The capacitor is made

up of a pair of concentric cylinders and has a stability of one part in 10^5 . Dielectric constant measurements are being combined with accurate density data to form the Clausius-Mossotti (CM) function, $1/\rho (\epsilon-1)/(\epsilon+2)$ which for ethane, like other non-polar fluids, is nearly independent of the temperature and density. This work has been very valuable for examining the consistency of the available density data for ethane, including the new equation of state (PVT) data discussed above and the new magnetic densimeter measurements discussed under "Densities of LNG Mixtures" below. Data analysis and report preparation are nearly complete.

7.3 Ethane, Specific Heat Data--H. M. Roder.

Specific heat data (C_v) are required to define accurately the derivatives of the equation of state (PVT), which in turn are used to calculate other thermodynamic functions such as enthalpy. Measured values of C_v are particularly valuable for cross-checking thermodynamic calculations for the compressed liquid states. We are preparing for a series of C_v and C_{SAT} measurements on ethane similar to those completed on methane under this program [1]. Measurements of the heat capacity of the empty calorimeter will be extended from 300 to 330 K to permit C_v measurements of compressed gaseous ethane at temperatures above critical. Since the critical temperature of ethane (305.3 K) is well above room temperature, fluid of relatively high density will reside in the filling capillary part of the system, and will have to be accounted for accurately.

During this reporting period the heat capacity apparatus has been checked out electrically, and for vacuum, and some heat capacity measurements have been made on the empty calorimeter. Accuracy and consistency checks on methane have been completed. Specific heat, C_{SAT} and C_v , measurements on compressed and liquefied ethane are in progress.

[1] B. A. Younglove, J. Research. NBS 78A, 401 (1974).

7.4 Ethane, Sound Velocity Data--R. Tsumura*

New ultrasonic measurements of the velocity of sound in compressed and liquefied ethane (90 - 320 K, 35 MPa (5000 psi)) are in progress. Preliminary measurements on saturated liquid ethane (90 - 305 K) have been completed. Preparations for measurements of the dependence of the sound velocity on the pressure and density are underway.

* Guest Worker, supported by a fellowship from Consejo Nacional De Ciencia Y Tecnologia (CONACYT), Mexico City, Mexico.

7.5 Ethane, Thermodynamic Properties Data--R. D. Goodwin.

Preparations for a substantially improved iteration of our provisional thermodynamic properties data for ethane, reported in NBSIR 74-398, "Provisional Values for the Thermodynamic Functions of Ethane," by R. D. Goodwin, are in progress. This second, and final, iteration will include all available new physical property measurements for ethane, obtained both as a part of this program and elsewhere, during the last two years. Comparisons between calculated and directly measured specific heats and sound velocity data mentioned previously in this report will also be included. Substantial improvements in the equation of state for ethane have been obtained.

1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

Principal Investigators. W. M. Haynes, M. J. Hiza, W. M. Parrish and R. D. McCarty, NBS, Boulder, Colorado 80302.

2. Cost Center Numbers. 2751574, 2752574

3. Sponsor. LNG Density Project Steering Committee, American Gas Association, Inc., Project BR50-11.

4. Introduction. Accurate density measurements and calculation methods for liquefied natural gas mixtures are needed to provide a basis for custody transfer agreements and for mass, density, and heating value gauging throughout the fuel gas industry.

The basis for the custody transfer of natural gas is its heating value. It is difficult to determine and agree on the heating value of extremely large volumes of natural gas in the liquid state. For example, methods for calculating the heating value of a liquefied natural gas mixture require knowing its density, which in turn depends on its composition, temperature, and pressure. As the compositions of LNG mixtures vary considerably, depending on the sources of the gas and the processing conditions, accurate methods are needed for calculating liquid densities at arbitrary compositions, temperatures and pressures. The accuracy is important because of the extremely large volumes of liquid involved.

5. Objectives or Goals. The objectives of this work are to perform accurate (0.1%) and precise (0.02%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures mainly in the temperature range 105 - 140 K, and to test and optimize methods for calculating the densities of LNG mixtures at arbitrary compositions and temperatures.

6. Background. This project is being carried out at NBS because of the realization that equitable custody transfer agreements could be reached more readily if the density measurements and the evaluation and development of calculation methods were performed by independent professionals of established reputation.

Prior to this reporting period an apparatus incorporating a magnetic suspension technique has been developed for absolute density measurements on liquids and liquid mixtures, particularly at saturation, for temperatures between 90 and 300 K. The repeatability and estimated precision of measurement are better than 0.02% while the accuracy is better than 0.1%.

7. Program and Results. Saturated liquid density measurements have been completed for the pure components of liquefied natural gas in the following temperature ranges: (a) methane (105 - 160 K); (b) ethane

(100 - 270 K); (c) propane (100 - 280 K); (d) normal butane (135 - 300 K); (e) isobutane (115 - 300 K); and (f) nitrogen (95 - 120 K).

Comprehensive accurate density measurements on selected binary mixtures of LNG components are in progress. Accurate density measurements on multicomponent (≤ 6) mixtures of LNG components have been initiated.

The evaluation and optimization of predictive calculation methods for the densities of LNG mixtures are in progress.

1. Title. LNG DENSITY REFERENCES SYSTEM

Principal Investigator. Ben Younglove
NBS, Boulder, Colorado 80302.

2. Cost Center Number. 2751361

3. Sponsor. American Gas Association, Inc.
Project BR-50-10.

4. Introduction. The emphasis of the LNG effort of NBS is in providing technical support to industry in meeting the energy needs of our economy with natural gas.

The density reference system will evaluate the ability of commercially available instruments to measure densities of LNG. Density is an essential measurement in performing total energy content determinations of natural gas reservoirs. This effort is oriented towards metrology and the output is correlated with cost center 2751574 which provides basic reference data on pure liquids and mixtures which will serve as density standards.

5. Objectives. This research will provide a system for evaluating the density measurement capability of commercially available meters. We will evolve a density reference system capable of generating accurate densities for this evaluation. From the commercial meters we will attempt to select one capable of performance as a transfer standard in order to provide traceability of accuracy to field density measurement systems.

6. Background. The density reference system was initiated in 1973 with a proposal to the AGA for research on LNG technology. Since that time the reference system has been selected, designed, constructed, and is now in operation, evaluating density metering systems.

7. Program and Results. The density reference system has shown consistent good agreement in density measurements to the densities of Haynes (ref. cost center 2751574) for liquid methane. That is, essentially all of the measurements are within 0.15% of Haynes.

Data on the performance of density measurement by the vibrating cylinder, vibrating plate, and capacitance meter in liquid methane have been taken.

The suppliers of the above densitometers have kept in close touch with the progress in evaluation of their meters. There has been some malfunctioning in these devices and some modifications made

The capacitance meter was altered by its design engineer to include a temperature sensor (platinum thermometer) and a new set of electronics for readout. This device now features readouts of density, temperature, and capacitance. The designer's intent is that the temperature sensor will allow a more accurate measurement of density over variations in hydrocarbon composition.

We have had input from the NBS statistical group as to statistical approaches for testing, they have also been of significant help in advising on detailed operation of the weighing head.

Colin McClune of Thornton Research Center (Shell Research Ltd.) has visited us and has given us the benefit of his knowledge on the qualitative behavior of two of the above devices. He intends to make further evaluations with his density system. It is our intention to keep in touch with his progress.

1. Title. HEATING VALUE OF FLOWING LNG
Principal Investigators. J. A. Brennan and J. M. Arvidson
NBS, Boulder, Colorado 80302.
2. Cost Center Number. 2756579
3. Sponsor. Pipeline Research Committee (American Gas Association) PR-50-48.
4. Introduction. This project will draw on information and facilities generated by other sectors of the NBS LNG effort. Thus, the calibration of a densitometer used will be traceable to the NBS density reference system being constructed by Younglove under cost center 2751361. Mixture density data produced under 2751574 by Haynes and Hiza will also provide a necessary input to the proper interpretation of results.
5. Objectives. The objective of this program is to measure the heating value of LNG flowing in a pipeline by the integration of individual measurements of flow, density and heating value. Flow measurement requires determination of flowmeter performance in line sizes larger than presently available calibration facilities. Therefore, a secondary objective is to establish appropriate flowmeter scaling laws.
6. Background. The LNG flow facility at NBS will be utilized to evaluate the response of the individual elements in the heating value measurement. Different compositions of LNG will be prepared to provide a range of densities sufficient to determine any dependencies. A limited amount of sampling work is included to determine the relative importance of this parameter to the overall measurement.

Flowmeter scaling is being done utilizing the cryogenic and the water flow facilities at NBS and private LNG peak shaving facilities. This portion of the program is behind schedule because of scheduling problems at the private LNG facilities.
7. Results. LNG Tests on the four-inch flowmeter that had been scheduled at an industrial LNG plant for early 1975 were not completed because there was no LNG send out. It now appears that a brief test might be possible during late November or early December 1975. Therefore, this critically important phase of the program has been delayed approximately one year from the original plan. In order to keep the delay in the flowmetering phase of the program as short as possible it was decided to go ahead with the necessary plans for the next larger size flowmeter (eight inch) and try to test both sizes during the next send-out season.

1. Title. LNG FUELS SAFETY
Principal Investigators. Neil A. Olien and A. F. Schmidt
NBS, Boulder, Colorado 80302.
2. Cost Center Number. 2750427
3. Sponsor. National Aeronautics and Space Administration, Cleveland, Ohio, Aerospace Safety Research and Data Institute.
Order No. C-39327-C.
4. Introduction. The NASA-Aerospace Safety Research and Data Institute (ASRDI) was established to provide a focal point for information and research in aerospace safety. One of the areas of concern for ASRDI is Cryogenic Fluid Safety. In fact, this was the first area of effort for ASRDI. The thrust of the program is two-fold: first, to provide an automated information bank for retrieving references, and second, to publish series of state-of-the-art reviews. The information system is now operational and contains over 7000 references in cryogenic fluid safety. In addition, ASRDI has published approximately twenty reviews.

Until this time, ASRDI has focused its attention and efforts on the two primary cryogenic propellants, hydrogen and oxygen. The oxygen work was started at NBS-Boulder in 1970 and the hydrogen work in 1972. With the coming possibility of methane or LNG fueled aircraft and the close affinity of LNG safety and cryogenic safety, ASRDI felt that it was timely to begin work in that area.
5. Objectives or Goals. The following objectives are to be achieved:
 - a) Review and modify an existing Cryogenic Fluids Safety Grid and thesaurus to include and adequately cover LNG safety.
 - b) Make a thorough search of over eleven information sources for LNG information. This will include published and unpublished material.
 - c) Catalog, index, abstract and put into machine readable form all available documents located in b) above. The indexing will be done by technical personnel with demonstrated competence in cryogenic safety and related fields.
6. Background. This program was started at NBS-Boulder by ASRDI in 1970. Since then considerable skill and experience has been gained in locating, processing and, most important, detailed subject indexing of safety-related information. In addition, NBS-Boulder has been providing detailed coverage of the LNG field for the American Gas Association since early 1970. The present program, then, provides an opportunity for industry, government and the public to capitalize on the accumulated past efforts of two seemingly unrelated programs.

7. Program and Results. Under this and another ASRDI-funded program we have started a major review of the indexing and retrieval terminology which will be used in the Cryogenic fuels safety information system. This review will result in a thesaurus to be published by NASA. The review is complete and we are now in the process of editing and preparing the thesaurus in its final form. Publication has been delayed awaiting a decision as to publishing the thesaurus separately or combined with one in fire safety and one in the mechanics of structural failure. Most of the terminology unique to LNG safety is now incorporated into this thesaurus. Approximately 500 papers, reports, etc. have been carefully indexed, abstracted, cataloged and transmitted to ASRDI.

1. Title. ENERGY CONSERVATION POTENTIAL IN THE LNG INDUSTRY
Principal Investigators. D. B. Mann and T. M. Flynn
NBS, Boulder, Colorado 80302.
2. Cost Center Number. 2750103
3. Sponsor. NBS Office of Energy Conservation
4. Introduction. By the end of 1975, there will be 166 LNG projects around the world in operation, under construction, planned, or proposed.

Peak shaving accounts for the largest number of LNG facilities with 106 being completed within the U.S. This number includes 55 actual peak shaving plants (which include liquefaction, storage, and gasification equipment) and 51 satellite facilities (which consist of storage and gasification equipment, but no liquefier). These 106 plants comprise a total storage capacity of approximately 65 billion cubic feet (equivalent gas volume) and a total liquefaction capacity of approximately 295 million cubic feet per day.

The impact of energy shortages world wide has underscored the need to utilize this resource (LNG) as efficiently as possible. Therefore, this program has been undertaken to provide the measurements and data base necessary for energy conservation in the Liquefied Natural Gas (LNG) industry. It will identify sources and degree of thermodynamic losses incurred during liquefaction, shipping, storage, and regasification of LNG and assure an adequate cryogenic measurement methodology and data base to facilitate the most effective use of Liquefied Natural Gas.
5. Objectives. The objective of the project is to provide the technical basis for the planned management of the cryogenic aspects of liquefied natural gas to enable its more effective utilization and prevent its exploitation or neglect. It will include, for instance, thermodynamic analyses of representative LNG systems to define the thermodynamically "ideal" base for comparison to actual practice. It will identify and test instruments and measurement techniques in support of energy conservation, and analyze and test the feasibility of energy recovery through utilization of the cold in LNG.
6. Background. New project.
7. Program and Results. During this fiscal year, we completed the first four months of an intended three year study whose ultimate purpose is to provide the measurements and data base necessary for energy conservation in the Liquefied Natural Gas (LNG) industry. Progress made during these first four months include:
 - 1) An historical perspective of the LNG industry to identify trends,
 - 2) The selection of peak shaving as the first subject for study, including a description of the process and essential components;
 - 3) A thermodynamic analysis of the peak shaving process;
 - 4) An identification of the most pressing measurement and instrumentation needs.

Specific objectives during this first period were to provide:

- 1) A documentation and definition of the LNG industry.
- 2) An LNG peak shaving process description.
- 3) A description of the variations among LNG peak shaving process components.
- 4) Thermodynamic analysis -- reversible process.
- 5) Thermodynamic analysis -- limitations.
- 6) Thermodynamic analysis -- applications to existing facilities.
- 7) An analysis of energy conservation through the potential of refrigeration recovery, or cold utilization.
- 8) An identification of tentative measurement instrument needs.
- 9) A base for measurement development for conservation requirements.

Among our first conclusions are the following:

- 1) LNG peak shaving is an established and growing U.S. industry.
- 2) Much technical information is already available for conservation analysis.
- 3) The peak shaving process is subject to analysis using classical thermodynamics.
- 4) It is possible to establish a thermodynamically reversible process as an ideal, to measure real processes against.
- 5) Some irreversibilities are dictated by external requirements of the process (e.g., vaporization for rapid send out).
- 6) Liquefaction is the largest single irreversibility, followed by storage losses.
- 7) Process efficiencies could be further enhanced if it were possible to build an integrated plant where cold utilization were a coordinated objective.
- 8) Tentative measurement requirements identified are: thermometer, densitometer, flowmeter, liquid level and mixture fraction, all in gas or cryogenic liquid phases.
- 9) Some thermodynamic, electrodynamic, transport, and phase equilibrium properties data are inadequate as of the reporting period. Existing experimental and analytical programs on property data will eliminate this inadequacy within the scope of the three year study.

1. Title. SURVEY OF CURRENT LITERATURE ON LNG AND METHANE
Principal Investigator. Neil A. Olien
NBS, Boulder, Colorado 80302.
2. Cost Center Number. 2750362
3. Sponsor. American Gas Association Project BR-50-10.
4. Introduction. It is important that all NBS personnel working in LNG, as well as the AGA and others, keep up with what is going on throughout the world in the LNG field. This project is designed to provide the Current Awareness and other information services to allow workers to keep abreast of new research and other developments.
5. Objectives or Goals. We will publish and distribute each April, July, October and January a listing of all significant papers, reports and patents relating to methane and LNG properties and technology. The references will be listed under convenient subject headings. The Quarterly will be distributed to all interested AGA member companies and be made available to the general public on a subscription basis. In addition, LNG related information will be entered into the Cryogenic Data Center's Information System for quick retrieval. A continuing awareness of the current publication scene will be maintained for any new periodicals to be reviewed cover-to-cover. Finally we will update and make available comprehensive bibliographies on the properties and technology of LNG. There are three bibliographies involved: methane properties, methane mixtures properties, and processes and equipment involving methane and LNG. These three will be updated each October.
6. Background. In 1969 we made a thorough review of the world's publications to determine which periodicals and abstracting services should be scanned cover-to-cover to adequately encompass the LNG field. The result is that we now scan over 300 primary publications and nearly 30 secondary publications. Of these approximately one-third are directly related to LNG. In addition, within the past year we have increased our coverage of the energy field to include hydrogen as a future fuel. Much of this information is also pertinent to LNG and as such is listed in our LNG-related publications. Our Current Awareness Service has been published weekly since 1964 (beginning in 1975 the publication became biweekly) and the Liquefied Natural Gas Survey has been published quarterly since 1970.
7. Program and Results. Four issues of the LNG Quarterly are prepared each year and distributed. There are now 120 subscriptions going to AGA Member Companies and 168 to other subscribers.

The three comprehensive bibliographies mentioned in section 5 have been reviewed and shorter, more selective bibliographies have resulted. These were prepared in January 1975.

- B-1262 THE THERMOPHYSICAL PROPERTIES OF METHANE AND DEUTERO-METHANE IN THE SOLID, LIQUID AND GASEOUS PHASES - A SELECTED BIBLIOGRAPHY. Indexed by property, phase and author, 68 pages (Feb 1975). (\$8.00).
- B-1263 THE THERMOPHYSICAL PROPERTIES OF METHANE MIXTURES - A SELECTED BIBLIOGRAPHY. Indexed by property, system and author, 118 pages (Feb 1975). (\$10.00).
- B-1264 PROCESSES AND EQUIPMENT INVOLVING LIQUEFIED NATURAL GAS AND METHANE - A SELECTED BIBLIOGRAPHY. Indexed by subject and author, 76 pages (Feb 1975). (\$8.00).

These are being updated now and will be available in January 1976. Over the past five years we have distributed over 400 copies of these and the comprehensive bibliographies. A bibliography on LNG Patents was supplied to AGA in May, 1975. A supplement to this was completed in July.

1. Title. CRYOGENIC DATA CENTER INFORMATION SERVICES
Principle Investigator. Neil A. Olien
NBS, Boulder, Colorado 80302.
2. Cost Center Numbers. 2750121, 2750126
3. Sponsor. NBS-Institute for Basic Standards and NBS-Office of Standard Reference Data.
4. Introduction. The need for information services in science and technology has spawned several kinds of activities. One of these is the Information Analysis Center (IAC). The Cryogenic Data Center is one of over one-hundred IAC's. A typical IAC, whether it is mission or discipline oriented, is concerned with obtaining all information and data in a given area and then performing data evaluation of a particular subset of that data. In the case of the Cryogenic Data Center the field is physics and engineering below 150 K with data analysis performed on the low temperature properties of fluids. In most cases, the data evaluation is done critically and the resulting data compilation is recognized as Standard Reference Data.
5. Objectives or Goals. We will publish and distribute a Biweekly Current Awareness Service listing references to new published papers in the fields of low temperature physics and chemistry and cryogenic engineering. Literature on the properties of the Industrially Important Gases will be identified and listed regardless of temperature range. In addition associated areas in the energy field will be covered. All important information will be thoroughly indexed and cataloged and entered into an automated information storage and retrieval system. Searches of this system will be made on demand. Fluid properties papers will be indexed in greatest depth so as to efficiently identify source data for evaluation projects throughout the world. Literature searches utilizing the automated system will be made on demand in answer to specific requests from NBS, other government agencies, universities and the general public. Three quarterly subscription services will be printed and distributed. These all "Superconducting Devices and Materials," "Liquefied Natural Gas" and "Hydrogen-Future Fuel." Charges will be made for Data Center services on a cost reimbursable basis.
6. Background. The Cryogenic Data Center was established in 1958 to serve as a central source of information on the properties of materials at cryogenic temperatures and to evaluate data on the properties of the cryogenic fluids. In 1963 the Center became a charter member of the National Standard Reference Data System with the establishment of the Office of Standard Reference Data within NBS. In addition contact has been established with fluid properties evaluation groups throughout the world and with other, similar information centers. The staff of the Center have pioneered in the application of advanced statistical techniques in the development and optimization of empirical equations of state and in the prediction of transport

properties by means of potential functions based on thermodynamic data. In the area of documentation, the Center has adapted state-of-the-art techniques in the development of its computerized information system. Highly skilled and experienced professionals are used in all subject indexing functions.

7. Program and Results. The Current Awareness Service has been published since 1964 and currently goes to over 400 subscribers. Subscriptions and marketing are handled by the National Technical Information Service. New marketing techniques have been and are being explored and implemented to increase the sales of the products handled by NTIS. The Superconducting Devices and Materials Quarterly has been published since 1968 and is prepared in cooperation with the Naval Research Laboratory, the NBS-Cryoelectronics Section, the Office of Naval Research and Superconducting Technology, Incorporated. There are currently 240 subscribers. The Liquefied Natural Gas Quarterly has been published since 1970 in cooperation with the American Gas Association and has 288 subscribers. The Hydrogen-Future Fuel Quarterly was started in August 1973 and is now sent to 192 individuals and firms. The automated information system contains over 100,000 carefully indexed papers in such areas as properties of fluids, properties of solids, processes and equipment, patents, instrumentation and metrology, etc. Over 150 major bibliographies are prepared each year and other requests are distributed approximately as follows: Visitors and telephone requests for information and data - 135 per year; letter requests for information, data and technical advice - 480 per year; requests for reprints, reports and other publications - 770 requests each year for over 3200 documents.

Data evaluation work has concentrated on the thermodynamic and transport properties of primarily the elemental gases. Compilations representing Standard Reference Data have been published for hydrogen, helium, nitrogen, oxygen, fluorine, neon, and argon. In addition, a number of specialized data sets have been prepared for such things as the solid properties of the isotopes of hydrogen and custody transfer data for four industrial fluids. The techniques developed and experience gained with pure fluids is now being extended to the development of predictive calculational methods for fluid mixtures. The goal is to develop mixtures equations of state which will be based on pure fluid and binary mixture data only. The mixtures work is in a very preliminary stage.

1. Title. ANALYSIS, EVALUATION, AND COMPILATION OF CHEMICAL
THERMODYNAMIC DATA

Principal Investigator. D. D. Wagman
Chemical Thermodynamics Data Center
Physical Chemistry Division
National Bureau of Standards
Washington, D. C. 20234

2. Cost Center Number. 3160115

3. Sponsor. Office of Standard Reference Data, NBS

4. Introduction. The Chemical Thermodynamics Data Center is concerned with the systematic development of a set of self-consistent values for the standard enthalpies, Gibbs energies and entropies of formation at 298°C of nearly all inorganic substances for which data are available and for organic compounds having at most 2 carbons in a chain. The data considered include all phases and many aqueous solutions especially those of electrolytic systems. It is clear that a large number of fluids is included even when the electrolytic solutions are excluded from consideration.

5. Objectives or Goals. The objective of this project is the development of a self-consistent set of standard enthalpies, entropies and Gibbs energies of formation at 298°C for as many substances as possible including their aqueous solutions.

6. Background. The standard enthalpies, Gibbs energies and entropies are the primary thermochemical properties needed to calculate the equilibrium constants for chemical reactions which determine the maximum yields which may be obtained. These properties are also useful for determining the heat that must be supplied to carry on a reaction or alternatively the heat generated in the reaction (heat which usually must be removed to maintain control of the temperature of the reactor). The standard properties at 298°C form the basic matrix of properties used. These must be corrected for changes in temperature away from 298°C and for solvent effects and nonideality of mixing for maximum accuracy; however, they are always needed and often give revealing information even without detailed correction.

7. Program and Results. The center is covering the substances for which data are available in a systematic fashion. The elements of the periodic table are considered according to an ordering developed for the purpose. At each stage, the element is considered along with any compounds it might make with elements occurring earlier in the ordering system.

Most of the periodic table has been covered at this time, the exceptions being the alkali metals and the actinide elements. These are being worked on concurrently and should be finished within 18 months. When these two sets of substances are completed, there will be a complete set of self-consistent data for substances for which measurements are available covering the entire periodic table.

This center also contributes the inorganic section and the editing for the Bulletin of Thermodynamics and Thermochemistry which is a bibliographic collection indexed by substance and property which is issued yearly.

Title. THERMODYNAMIC DATA ON ORGANIC COMPOUNDS

Principal Investigator. Bruno J. Zwolinski
Texas A&M University
FE Box H
College Station, Texas 77843

Cost Center Number. 1510200

Sponsor. Office of Standard Reference Data, NBS

Introduction. This data center has a long history of compilation and evaluation of data on organic compounds starting with the beginning of API Project 44, some 30 years ago. The API interest was focussed on hydrocarbons and related substances found in petroleum, and work on these substances under API sponsorship continues to the present. The center has had support from the OSRD over the last 10 years to cover other types of organic substances.

Objectives or Goals. The objective of this project is the provision of critically evaluated reference data on selected thermodynamic and thermophysical properties for selected scientifically and industrially important organic chemicals.

Background. The properties covered by the center in its various projects for the OSRD include ideal-gas thermal functions, properties of the real gas, enthalpies and entropies of formation, vapor pressures and transition temperatures, densities and refractive indices. The substances chosen for study have scientific and/or industrial importance. The properties covered are those properties needed to determine the equilibrium behavior of the substances in question under the conditions met with in chemical processing plants.

Program and Results. Recent results have included a definitive work on the properties of the aliphatic alcohols, which was published as a Supplement of the Journal of Physical and Chemical Reference Data, and a series of papers on the ideal-gas properties of the halogenated hydrocarbons.

At the present time, the center has undertaken to produce a self-consistent set of thermochemical properties for a set of oxygen-containing compounds having one to four carbon atoms. The set includes representatives of major homologous series such as alcohols, acids, ketones, ethers. There are perhaps 15 compounds for which extensive data exist. Not only will the results provide evaluated data on the initial compound or two of important homologous series, but the data will be consistent with the thermodynamic changes observed when these compounds are changed one into the other by chemical processes such as oxidation and reduction.

Since the compounds for which data exist are of industrial importance, the data resulting from the project will be important in their own right for industrial purposes and will serve as the basis for estimation techniques, such as are used to estimate the properties of higher homologs through the addition of methylene groups.

In addition, the center contributes to the Bulletin of Thermodynamics and Thermochemistry which is a bibliographic collection indexed by substance and property which is issued yearly.

Title. JOINT INDUSTRY-GOVERNMENT PROJECT ON THE
THERMOPHYSICAL PROPERTIES OF ETHYLENE

Principal Investigators.

D. R. Douslin, ERDA Energy Research Center, Bartlesville,
Oklahoma

M. Klein, Equation of State Section, Heat Division,
NBS, Gaithersburg, Maryland

R. D. McCarty, Cryogenic Data Center, NBS, Boulder, Colorado

J. Powers, University of Michigan, Ann Arbor, Michigan

H. J. White, Jr., Program Manager, Office of Standard
Reference Data, NBS, Gaithersburg, Maryland

Cost Center Numbers. 1510404, 1510430, 2750128, 3104575

Sponsors. Office of Standard Reference Data, NBS

Industrial Sponsors Group

Celanese Chemical Company

Cities Service Oil Company

Continental Oil Company

Gulf Research and Development Company

Mobil Chemical Company

Monsanto Polymers & Petrochemicals Company

Phillips Petroleum Company

Union Carbide Corporation

Introduction. Ethylene is one of the most extensively used chemicals in the world, current US usage running in the vicinity of 25 billion pounds per year. In addition to being handled on a large scale at plant sites, ethylene is transported in large quantities by pipeline and cryogenic tank ship. The PVT and related thermodynamic properties are used for process and equipment design, process and plant control, instrumental analysis and custody transfer. However, at the present time there is no authoritative wide-ranging formulation of these properties of sufficient accuracy and precision to serve all of these purposes. Furthermore, it is not possible to obtain one without additional experimental measurements to fill gaps and resolve contradictions in the existing data. This project was initiated to obtain such a formulation.

Objectives or Goals. The objective of this project is to prepare an authoritative, comprehensive and self-consistent set of PVT and thermodynamic properties of ethylene to within the accuracy and precision allowed by the state of the art (0.1% in density).

6. Background. Requirements were established and the technical program needed to meet them were specified in a series of meetings with industrial representatives. Broadly based industrial support and cooperation were needed to insure products appropriate to industrial practices and widespread acceptance of the results. It was also necessary that those doing the work be expert in carrying out the experimental measurements and data evaluation required. Finally, it was necessary that the project be so organized that it would be free from possible bias from special interests. A joint project involving industrial and governmental support under the program management of the Office of Standard Reference Data seemed to meet these various requirements and was established in 1974.
7. Program and Results. The project is scheduled over a five-year period, and is into its second year. Measurements have been completed which define the critical point and the behavior in the critical region very accurately. The next phases of the work will deal with the properties of the vapor and liquid at temperatures between the critical and the triple point. Data evaluation is being carried out concurrently with the experimental program.

Title. EXCESS PROPERTY DATA FOR BINARY LIQUIDS

Principal Investigator. Buford D. Smith
Thermodynamics Research Laboratory
Washington University
St. Louis, Missouri 63130

Cost Center Number. 1510297

Sponsor. Office of Standard Reference Data, NBS
and industrial sponsors

Introduction. The Thermodynamics Research Laboratory carries out a program of compilation and evaluation of data from the literature, experimental measurement, and the development of computer programs for correlation and computation of data needed by industry. The fields covered are the excess volume, heat of mixing and vapor-liquid equilibrium of binary non-electrolyte systems. There are several sources of support; however, the program on compilation and evaluation of data from the literature, which is of primary interest here, receives support from the Office of Standard Reference Data and industry.

Objectives or Goals. The objectives of this project are the compilation and evaluation of a comprehensive set of data from the literature on the volume change on mixing, the heat of mixing and the vapor-liquid equilibria for binary systems in which both components are below their critical temperatures and neither is an electrolyte.

Background. The chemical industry is continually concerned with the properties of mixtures and the separation of these mixtures into separate components (for example, product and by-products). The properties compiled and evaluated by this center are those required for calculations needed in the design of distillation columns, for example. The compilation of a comprehensive set of evaluated data for binary systems will not only be useful in process and design calculations but will provide basic reference data for the needed development of more successful equations for interpolating, extrapolating and estimating the properties of solutions.

Program and Results. The center has developed a set of criteria for screening data found in the literature according to three criteria: the degree to which the data on vapor-liquid equilibrium are consistent with the Gibbs-Duhem relationship, the extent to which data for binary systems extrapolate to the evaluated data for the individual components and the scatter of the data. These criteria do not represent a

complete evaluation of the data; however, all good data must pass this screening and such a screening should be useful for many purposes, particularly in cases where the data available are limited.

The center plans over a period of time to cover all classes of binary systems for which data are available. Specific classes to be covered in the immediate future are:

1. C_3 plus heavier hydrocarbons (up to C_8)
2. C_4 plus heavier hydrocarbons (up to C_8)
3. Alcohols (C_1 through C_4) plus hydrocarbons (C_3 through C_8)

Title. THERMAL CONDUCTIVITY OF SELECTED SUBSTANCES

Principal Investigators. Y. S. Touloukian
C. Y. Ho
Thermophysical Properties Research
Center
Purdue University
Lafayette, Indiana 47907

Cost Center Number. 1510262

Sponsor. Office of Standard Reference Data, NBS

Introduction. This center is a major data center with support from a number of sources. It compiles data on specific heat, thermal conductivity, viscosity, thermal expansion and thermal radiative properties. Other centers allied with it in the Center for Information and Numerical Data Analysis and Synthesis compile data on other properties, in particular electrical conductivity which is of importance for the project considered here. In addition to compilation of data on a variety of properties for a wide range of substances, the center carries out data evaluation with the support of the Office of Standard Reference Data for selected properties and substances.

Objectives and Goals. The objectives of this project are to provide critically evaluated data on selected properties of selected substances. The evaluation has been focussed primarily on data for the thermal conductivity of metals and alloys to date.

Background. The properties covered by this center are those needed to understand and predict the transfer of heat from one place to another in a physical system. As such, they are needed in the design of processes and equipment whenever transfer of heat is anticipated, whether it is the input of heat to initiate or maintain a given process or the removal of unwanted waste heat.

Program and Results. The primary initial task of this center was the compilation and evaluation of the data for the thermal conductivity of the elements. This work culminated in a definitive text which was published as a Supplement to the Journal of Physical and Chemical Reference Data.

More recently, the work has been concerned with the thermal conductivity of a set of binary alloys. This work has required development of methods for interpolating among temperature ranges and between concentration ranges. A necessary adjunct has been compilation and evaluation of data on electrical conductivity and thermoelectric power for the same alloys and their individual components.

One further project of importance is the compilation and evaluation of data on the viscosities, thermal conductivities, and heat capacities of 73 fluids selected for their industrial importance. The fluids and the extent to which there are data on their properties are shown on the accompanying sheet.

R. No.	Name	VISCOSITY			THERMAL CONDUCTIVITY				SPECIFIC HEAT AT CONSTANT PRESSURE			
		LIQUID	VAPOR	GAS	SOLID	LIQUID	VAPOR	GAS	SOLID	LIQUID	VAPOR	GAS
	Acetone			x		x		x		x		x
	Acetylene			x				x				x
729	Air	x	x	x		x	x	x		x	x	x
717	Ammonia	x	x	x		x	x	x		x	x	x
740	Argon	x	x	x	x	x	x	x		x	x	x
	Benzene			x		x		x		x		x
	Boron Trifluoride			x				x		x		x
	Bromine			x		x	x	x		x		x
600a	iso-Butane	x	x	x		x	x	x		x	x	x
600	n-Butane	x	x	x		x	x	x		x	x	x
744	Carbon Dioxide	x	x	x		x	x	x		x	x	x
	Carbon Monoxide			x		x		x		x		x
10	Carbon Tetrachloride			x		x		x		x		x
14	Carbon Tetrafluoride			x		x	x	x		x	x	x
	Chlorine			x		x	x	x		x		x
20	Chloroform			x		x		x		x		x
	n-Decane					x		x		x		x
	Deuterium			x		x	x	x		x		x
170	Ethane	x	x	x		x	x	x		x	x	x
	Ethyl Alcohol (Ethanol)			x		x		x		x		x
610	Ethyl Ether			x		x		x		x		x
1150	Ethylene	x	x	x		x	x	x		x	x	x
	Ethylene Glycol					x				x		
	Fluorine			x		x	x	x		x		x
	Glycerol					x				x		
704	Helium 4			x	x	x		x		x	x	x
	n-Heptane			x		x		x		x		x
	n-Hexane			x		x		x		x		x
702	Hydrogen, normal	x	x	x	x	x	x	x		x	x	x
702	Hydrogen, para					x	x	x		x	x	x
	Hydrogen Chloride			x				x		x		x
	Hydrogen Iodide			x				x		x		x
	Hydrogen Sulfide			x				x		x		x
	Iodine			x	x	x	x	x				
	Krypton			x	x	x	x	x		x		x
50	Methane	x	x	x		x	x	x		x	x	x
	Methyl Alcohol			x		x		x		x		x
40	Methyl Chloride	x	x	x		x	x	x		x	x	x
720	Neon	x	x	x	x	x	x	x		x	x	x
	Nitric Oxide			x				x		x		x
728	Nitrogen	x	x	x	x	x	x	x		x	x	x
	Nitrogen Peroxide			x		x		x		x		x
744a	Nitrous Oxide			x				x		x		x
	n-Nonane					x		x		x		x
	n-Octane			x		x		x		x		x
732	Oxygen	x	x	x		x	x	x		x	x	x
	n-Pentane			x		x		x		x		x
290	Propane	x	x	x		x	x	x		x	x	x
1270	Propylene	x	x	x		x	x	x		x	x	x
	Radon					x	x	x				
11	R11 (Trichlorofluoromethane)	x	x	x		x	x	x		x	x	x
12	R12 (Dichlorodifluoromethane)	x	x	x		x	x	x		x	x	x
13	R13 (Chlorotrifluoromethane)	x	x	x		x	x	x		x	x	x
13B1	R13B1 (Bromotrifluoromethane)	x	x	x		x	x	x		x	x	x
21	R21 (Dichlorofluoromethane)	x	x	x		x	x	x		x	x	x
22	R22 (Chlorodifluoromethane)	x	x	x		x	x	x		x	x	x
23	R23 (Trifluoromethane)	x	x	x		x	x	x		x	x	x
113	R113 (Trichlorotrifluoroethane)	x	x	x		x		x		x	x	x
114	R114 (Dichlorotetrafluoroethane)	x	x	x		x		x		x	x	x
115	R115 (Chloropentafluoroethane)	x	x	x		x		x		x	x	x
142b	R142b (Chlorodifluoroethane)					x				x	x	x
152a	R152a (Difluoroethane)					x				x	x	x
216	R216 (1, 3-Dichloro-1, 1, 2, 2, 3, 3, - hexafluoropropane)					x				x	x	x
318	R318 (Octafluorocyclobutane)	x	x	x		x		x		x	x	x
500	R500 (R12, R152a azeotrope)	x	x	x		x				x	x	x
502	R502 (R12, R115 azeotrope)	x	x	x		x	x	x		x	x	x
503	R503 (R13, R23 azeotrope)					x				x	x	x
504	R504 (R12, R115 azeotrope)	x				x				x	x	x
761	Sulfur Dioxide			x		x		x		x		x
	Toluene			x		x		x		x		x
	Trichloro					x						
718	Water	x	x	x		x	x	x		x	x	x
	Xenon			x	x	x	x	x		x		x

1. Title. TRANSPORT PROPERTIES OF FLUIDS IN THE CRITICAL REGION

Principal Investigator. J. V. Sengers
University of Maryland
College Park, Maryland 20742

2. Cost Center Number. 1510286

3. Sponsor. Office of Standard Reference Data, NBS; NASA

4. Introduction. The region in the vicinity of the critical point is of particular importance for both the equilibrium and transport properties of fluids. Many properties change rapidly and substantially in magnitude as the critical point is approached. These changes are of technological importance for processes that approach or include the critical region. Furthermore, properties in the critical region and the critical constants themselves are used as base points and constants for data reduction for a variety of extrapolation and estimation procedures. As a result, methods for evaluating data in the critical region and for obtaining reliable self-consistent sets of data are of considerable importance. The importance of the evaluation procedures is increased by the difficulties met in making the experimental measurements.

5. Objectives or Goals. The objectives of this project are the development of methods for obtaining self-consistent, reliable sets of data for thermodynamic and transport properties in the vicinity of the critical point and formulations for the data in this region that are soundly based theoretically, make economical use of adjustable parameters and join smoothly with the classical formulations for these properties known to hold well away from the critical region.

6. Background. The critical region has been of unusual importance for many years. The rapid and substantial changes of many properties and the successful use of critical constants or properties for a variety of data-reduction processes have assured the practical importance of the region. At the same time, lack of understanding of the properties in this region and their apparent failure to follow classical theory have assured theoretical interest. Recent theoretical developments have given broader insight and have offered methods for analyzing data points in the critical region and comparing and correlating the results of different types of measurements. that are simple in form and economical in their use of adjustable parameters. These so-called "scaling law" methods thus offer the opportunity to develop self-consistent data sets for the critical region and formulations that describe the region accurately and with sparing use of constants.

Program and Results. Results already obtained include a method of separating the thermal conductivity in the vicinity of the critical point into a "normal" portion that reflects the behavior to be expected as a result of behavior well away from the critical region and an "excess" portion reflecting the change in behavior resulting from the proximity of the critical point. A method for describing the asymptotic behavior of the excess portion in the vicinity of the critical point has been developed as has a relationship between the thermal conductivity and the compressibility near the critical point so that mutually consistent data for the two properties can be obtained.

The program to be accomplished includes compilation and critical evaluation of thermal conductivity data for those fluids for which experimental data in the vicinity of the critical point are available, development of interpolation methods in the critical region and development of methods of joining the asymptotic behavior near the critical point with the normal behavior well away from the critical point.

1. Title. THERMODYNAMIC PROPERTIES OF FLUIDS

Principal Investigators. J.M.H. Levelt Sengers, L. Haar
Equation of State Section, Heat Division
National Bureau of Standards
Washington, D. C. 20234

2. Cost Center Numbers. 2210143, 2210147, 2214443

3. Sponsors. NBS, U.S. Navy, Office of Standard Reference Data-NBS

4. Introduction. The thermodynamic properties of fluids have been a long-term interest of the Heat Division of NBS. This interest results from the needs for such data for the handling and use of industrially important fluids and for the use of various fluids as working fluids in engines, heat exchangers, refrigerators, and the like. Overall needs for data on fluids encompass not only single fluids but multicomponent fluids and chemically interacting fluids as well. Similarly, the conditions of interest include some that are difficult or perhaps impossible to achieve and control in a research laboratory. Therefore, the activities of the Heat Division have covered a wide range of conditions and types of fluids.

5. Objectives and Goals. The objective of this project is the production of tables of thermodynamic properties of single and multicomponent fluids under a variety of equilibrium conditions including those difficult or impossible to reach under laboratory conditions.

6. Background. To reach the objectives of this project, it is necessary to examine all of the aspects of thermodynamic tables in detail. It is essential to study the foundations of theoretical descriptions, to determine the utility and meaningfulness of methods used for obtaining the parameters associated with such descriptions, to develop and improve theoretical models and to study the techniques used in the statistical analysis of data needed to obtain information from experiment. This comprehensive approach to the development of thermodynamic tables allows a clearer understanding of the reliability of such tables, leads to the avoidance of such pitfalls as the "overfitting" of individual sets of data and permits the use of such statistical mechanical constructs as intermolecular potentials in the development of tables of numerical data.

7. Program and Results. A correlation for the properties of ammonia has been completed and is being prepared for publication. This correlation extends considerably the range of the previous correlation for ammonia which is nearly 50 years old.

Computations of the composition and thermodynamic properties of air to 15,000 K for densities to 1000 times normal sea level density have been completed. At the highest temperatures, due to the dissociation and recombination of species, air consists of more than 30 reacting species. The problem is then one of calculating compositions and properties of a reacting gaseous mixture to very high densities - a general problem of some practical importance in explosives. Since the temperatures involved are well outside the range of experiment, the computational results cannot be checked directly. The results are nevertheless very illuminating. Of particular interest is the behavior of the different species concentrations relative to each other as functions of pressure. Details are included in a report to be submitted for publication.

The feasibility and utility of representing the equation of state of fluid mixtures in field variables ($PT\rho$) have been studied. Also simple but fundamentally based equations of state have been developed and examined for applicability in extensions of fluid property descriptions to high pressures.

Ideal gas thermodynamic properties for water to 0.01% accuracy will be completed. An equation of state for dense gases with permanent dipoles is being applied to water at temperatures above $1.25 T_c$ and densities to 3 times the critical density. Results to date indicate the theory is consistent with the available data. A study of the thermodynamic data for fluid water over the entire range of T and P will be undertaken.

The extension of a generalized molecular theory of dense fluids to the treatment of mixtures will be given major emphasis.

1. Title. THERMODYNAMIC PROPERTIES OF FLUIDS IN THE CRITICAL REGION

Principal Investigator. J.M.H. Levelt Sengers
Equation of State Section, Heat Division
National Bureau of Standards
Washington, D. C. 20234

2. Cost Center Numbers. 2210140, 2210141, 2214441, 2210149

3. Sponsors. NBS, NASA, Office of Standard Reference Data-NBS

4. Introduction. The region of the PVT surface in the vicinity of the critical point is important to theoreticians because the underlying causes of the observed behavior are not understood and of practical importance because of the unusual behavior that occurs in this region and the extensive use of the critical constants in the reduction of data. For these reasons the interests of the Equation of State Section in this region are many and varied and include experimental and theoretical work, data evaluation, and work on critical behavior in one component and multi-component systems.

5. Objectives and Goals. The objective of these projects is to carry out those measurements necessary to obtain an understanding and description of the behavior of fluid systems in the vicinity of phase transitions including one-component fluids and fluid mixtures.

6. Background. An understanding of the behavior of fluids near their critical points is of considerable importance in describing their properties over the entire space of thermodynamic states. The critical point is used as a point of symmetry for the reduction of thermodynamic data in corresponding states approaches. Such methods are of considerable utility in engineering calculations and, especially, in engineering predictions of properties of materials for which no measured data exist. Critical behavior is exhibited in such diverse systems as pure fluids, liquid mixtures, ferromagnets, ferroelectrics, order-disorder transitions in alloys, glasses, etc. Because these appear to be describable by the same formalism, an understanding obtained of one will be transferable to the description of another. Thus, the objective of this work is to obtain a quantitative understanding and description of fluids and of fluid mixtures near their critical points.

7. Program and Results. The anomalous thermodynamic behavior of fluids near their critical points can be described in terms of scaling laws. Two critical region equations of state that

satisfy the scaling laws have been studied. These are the NBS equation and the Linear Model parametric equation. Each of the equations was fitted to experimental equation of state data for six fluids, namely He^3 , He^4 , Xe, CO_2 , O_2 , and H_2O . The two equations represented the experimental data in the range $|T - T_c|/T_c < 0.03$ and $|\rho - \rho_c|/\rho_c < 0.25$ equally well. The optimum critical exponents appear to vary little from substance to substance in agreement with expectations based on universality of critical behavior. The principle of universality was used to predict critical region parameters for nine additional fluids, including several for which only limited experimental information was available. These fluids were Ar, Kr, N_2 , H_2 , CH_4 , C_2H_4 , SF_6 , NH_3 and D_2O . A single "universal" equation was thus developed for the critical region of all fifteen fluids considered.

A practical representation of the properties of liquid-vapor equilibrium state has been obtained for the critical region of CO_2 - ethane. The work is being extended to other systems such as SF_6 - propane and propane-n-octane as well as to one phase states near the critical line.

In the experimental work on one-component fluids, two complementary experimental techniques are used - one a Burnett method modified to meet the special demands of critical region studies, and the other a laser interferometric approach. The laser interferometry experiment gives highly detailed and accurate results for the chemical potential versus density relation in the near vicinity of the critical point, a most natural relation on theoretical grounds.

The work on liquid mixtures thus far consists of measurements of liquid densities to a precision of 1 ppm using a magnetic densimeter. These density measurements allow investigation of the critical exponents α and β and, to some extent, the effect of gravity on their determination.

Studies are being made on the roles of nucleation, diffusion and gravitational sedimentation upon the process of phase separation in pure fluids and fluid mixtures. Other studies are being conducted to define exploratory measurements of critical point anomalies and phase separation phenomena in the vicinity of critical points of pure fluids and fluid mixtures in the low gravity environment of the proposed space laboratory. Studies have also been made to discover and eliminate or compensate for systematic errors in the laser interferometry experiment.

Pressure-vs-temperature measurements for ethylene have been made along four isochores above T_c , one within 1% of the critical density. On the other three isochores, measurements were made both in the one-phase region and along the metastable extension of each isochore in the two-phase region. We have analyzed our vapor pressure and critical isochore data with the help of the thermodynamic scaling laws and have derived values of the critical exponents α (0.10) and γ (1.19). We have been able to measure metastable pressures that lie far enough within the two-phase region to exceed the limit calculated for carbon dioxide, according to existing theories of homogeneous nucleation.

Plans for the immediate future call for completion of work on ethylene and completion of measurements on the thermal expansion and co-existence curve of mixtures of isobutyric acid and water which have been started recently, and measurements on hexane-perfluorohexane mixtures.

Title. PVT RELATIONS IN GASES

Principal Investigator. M. Waxman
Equation of State Section, Heat Division
National Bureau of Standards
Washington, D. C. 20234

Cost Center Number. 2210142

Sponsor. NBS

Introduction. If a fluid is to be used as a working fluid, as in a power generating plant, or is a principal component in a chemical process, a thorough knowledge of the PVT properties of the fluid is necessary for the design of equipment and processes of optimum efficiency. Such properties may also be needed for custody-transfer calculations. Specific examples of needs of these types involving ethylene and liquefied natural gas are detailed elsewhere in this report.

Meeting such needs requires the development of equipment and methods to make the necessary measurements, and to advance the state of the art to keep pace with the increasing needs of the industrial community. The experiments being carried out at the present time involve the use of ethylene and hence serve to provide support to the ethylene project, which is described elsewhere, as well as to lead to further development of the techniques involved.

Objectives or Goals. The objectives of this project are the measurement of the PVT properties of industrially important fluids with the precision allowed by the state of the art and the maintenance and enhancement of the capability to make such measurements as a long-term objective of the Heat Division.

Background. The PVT method used to determine the compressibility factors and virial coefficients is a simplified method introduced by Burnett in 1936. In this method neither the quantity of gas (n) nor the volume (v) is measured; instead, accurate isothermal pressure measurements are made before and after stepwise expansions between two volumes. This method leads to a decrease in the overall measurement error and can, in principle, lead to more accurate results than can be obtained from a method requiring the measurement of n and v . The results derived from this method are sensitive to the details of the non-linear data reduction procedures used to analyze the experimental data for which reason we have spent considerable time on problems of non-linear statistics.

Program and Results. Immediate objectives are: (a) to obtain isothermal Burnett PVT measurements on gaseous ethylene for the temperature range 0°C to 150°C and for pressures to 35 bar; (b) to calculate the compressibility factors and second virial coefficients for ethylene from Burnett measurements and to evaluate these results.

16. Abstract (continued)

This report has been prepared to show interested readers the interrelationships within a set of projects that might otherwise pass unnoticed because different organizational units within NBS are involved. Continued interaction between the program managers involved leads to interactions between the projects so that the listing is not a listing of independent unreacting projects but rather a listing of interacting projects following broad programmatic lines.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET		1. PUBLICATION OR REPORT NO. NBSIR 76-1002		2. Gov't Accession No.		3. Recipient's Accession No.	
4. TITLE AND SUBTITLE Industrial Process Data for Fluids: A Survey of Current Research at the National Bureau of Standards						5. Publication Date April 1976	
7. AUTHOR(S) Howard J. White, Jr., Editor						8. Performing Organ. Report No. NBSIR 76-1002	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234						10. Project/Task/Work Unit No.	
						11. Contract/Grant No.	
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) Same as No. 9						13. Type of Report & Period Covered Summary Report	
						14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES							
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) This report summarizes current activities sponsored by three groups within the National Bureau of Standards that are involved with the production of industrial process data for fluids. The three groups involved are the Cryogenics Division, the Equation of State Section of the Heat Division, and the Office of Standard Reference Data; other organizations in NBS and outside are also involved in various ways. The report takes the form of a listing of projects with some detailed information about each. Some of the projects are designed to provide industrial process data directly. Others systematically cover types of data that are of continual utility in industrial process calculations with the result that the data produced will be used for industrial purposes as well as for other purposes. A few of the projects attack problem areas that must be resolved before proper industrial process data in the area can be obtained. All of the projects focus on quantitative numerical data obtained for direct measurement, critical evaluation of data from the literature or theoretical estimation or calculation.							
(continued)							
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Industrial process data; project summaries; quantitative numerical data							
18. AVAILABILITY <input checked="" type="checkbox"/> Unlimited				19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED		21. NO. OF PAGES 54	
<input type="checkbox"/> For Official Distribution. Do Not Release to NTIS				20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED		22. Price \$4.50	
<input type="checkbox"/> Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13							
<input checked="" type="checkbox"/> Order From National Technical Information Service (NTIS) Springfield, Virginia 22151							

